Abstract No. Yang0274

The Structural Studies of the New Carbon Coated Silicon Anode Materials Using *In Situ* XRD

X.Q. Yang and J. McBreen (BNL), W-S. Yoon and C, Grey (SUNY, Stony Brook)

Beamline(s): X7A

Introduction: Almost all commercial lithium-ion batteries on the market today use carbonaceous materials for anodes. These carbonaceous materials offer good cycling performance. However, the theoretic capacity of these materials is only 372 mAh/g. Recent research in developing new anode materials includes studies of tin-, silicon- and intermetallic-based systems with a major goal of increasing the capacity. Si can form alloys with Li up to $Li_{4.4}Si$ at high temperature, which corresponds to a capacity as high as 4000 mAh/g. However, the reversibility of the Si powder is rather poor[1]. The new silicon-based system developed jointly by Yoshio *et al*[2] and Umeno *et al* [3] showed reversible capacity as high as 1000 mAh/g. This new type of silicon-based anode material was prepared by thermal vapor deposition (TVD). It is important to study the structural changes of this new material during cycling. The synchrotron based high resolution *in situ* XRD is a powerful tool to study the structural changes of electrode materials with long range ordering.

Methods and Materials: Samples are provided by Mitsui Mining Co. in Japan and the procedure of sample preparation was described elsewhere [2,3]. Samples with different C/Si ratios were used. The anode material was mixed with 10% carbon black and 10% PVdF first. The anode was made by slurrying the mixture with NMP solvent and then coating it on thin Cu foil. The active material of each cathode disk (2.8 cm^2) is about 15 mg. In situ XRD studies: In situ XRD spectra were collected on beam line X18A (using λ=1.54 Å wavelength) and X7A (using λ=0.7 Å wavelength) at National Synchrotron Light Source (NSLS). The spectroelectrochemical cell: All of the in situ data reported here were done in a spectroelectrochemical cell that has been described elsewhere. The counter electrode used was lithium foil. The window materials are Mylar films.

Results: Full XRD scans covering 2θ angles from 26 degrees to 58 degrees were recorded periodically. No new reflections were observed in these patterns. This indicates that no detectable amount of a new crystal structure was formed. The notable changes are the significant peak broadening and intensity reduction of the (111), (220), and (311) reflections. More severe peak broadening was observed when more lithium was intercalated into the anode material

Conclusions: These results indicate that the lithium intercalation in this new silicon powder material takes place by converting the silicon crystal into the amorphous state. The reversibility of the structural changes relating to the level of lithium intercalation. The local structure changes that occur during cycling are under investigation with lithium NMR spectroscopy.

Acknowledgments: The XRD measurements were carried out at X7A of NSLS. The work done at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division, USDOE under Contract Number DE-AC02-98CH10886. The work done at SUNY Stony Brook was supported by the National Science Foundation (DMR 9901308).

References:

1. R. A. Huggins, Solid State Ionics, 113-115, 57 (1998)
2. M. Yoshio, N. Dimov, T. Iwao, K. Fukuda, and T. Umeno Abstract 248, the 200th Meetings of the electrochemical Society, San Francisco, USA, September 2-7, 2001.
3. T. Umeno, K. Fukuda, H. Wang, N. Dimov, T. Iwao, and M. Yoshio, Chemistry Letters,1186-1187 (2001).